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TITLE: EVALUATION OF ATOMIC OXYGEN INTERACTION WITH THIN-FILM
ALUMINUM OXIDE

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EVALUATION OF ATOMIC OXYGEN INTERACTION WITH THIN-FILM ALUMINUM OXIDE

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ABSTRACT

Effects of atomic oxygen on thin-film (750Å) sputtered aluminum oxide (Al_2O_3) have been characterized. Experiments were conducted using the Los Alamos National Laboratory (LANL) O-atom facility. Diffusion of O-atoms through the Al_2O_3 thin films was observed, having an activation energy of 5.2 kcal/mole at an O-atom kinetic energy of 2eV. Silver oxidation was used as the technique to detect penetration of O-atoms through thin-films. The Al_2O_3 films were deposited on silver (250Å), and the electrical resistance of the silver was measured in-situ during exposure. The thin films provided better protection of the substrate when deposited on smooth sapphire surfaces than when deposited on rougher alumina surfaces. The Al_2O_3 was amorphous before and after exposure, with less than 2% variation in oxygen atomic concentration and total Al_2O_3 thickness before and after exposure.

INTRODUCTION

Experimental data from Space Shuttle flights have shown that atomic oxygen (AO), the primary constituent of the low Earth orbit (LEO) environment, reacts with many commonly used spacecraft materials.⁽¹⁻³⁾ Atomic oxygen, which has high oxidative ability, strikes ram surfaces with a collision energy of about 5 eV for spacecraft such as Space Shuttle travelling in LEO at a velocity of 8 km/sec. Organic materials, such as Kapton, polyethylene, and graphite/epoxy, were found to be susceptible to AO attack and subsequent erosion.⁽³⁾ Some metals, such as silver and osmium, were also oxidized by exposure to AO.⁽⁴⁾ Atomic oxygen degradation of materials, therefore, is a significant factor in the lifetime limit of spacecraft.

The planned life of the future Space Station, Freedom, is 20 to 30 years in LEO.⁽¹⁾ If AO reactive materials such as Kapton and graphite/epoxy are to be used as structural components, coatings will be needed to protect their surfaces from AO attack. Development of protective coating systems has been in progress for several years.⁽⁵⁻⁷⁾

We have conducted experiments on AO interaction with coatings at the Los Alamos National Laboratory (LANL) O-atom simulation facility.⁽⁸⁾ Several types of coatings, including metal oxides, Teflon, and silicones, were evaluated for protection of AO reactive surfaces.⁽⁹⁾ The results presented in this paper detail our characterization of AO effects on thin-film (750Å) aluminum oxide.

METHODS

A Technique to Evaluate Coatings for Atomic Oxygen Protection

The technique employed in our evaluation of coatings uses silver oxidation as a detector for AO penetration through coatings.⁽¹⁰⁾ Silver oxidizes rapidly in the presence of AO to form silver oxide, and the electrical resistance of the oxide is much higher than that of pure silver. In our technique to evaluate coatings for AO protection, coatings of known thickness are first deposited over thin (250Å) silver films, and then the electrical resistance of the silver is measured in-situ during exposure to detect when the AO penetrates the coating.

A schematic of the sensors used is shown in Figure 1. The sensor consists of two strips of silver (250Å) deposited on top of a substrate (made of alumina or sapphire). One of the silver strips is coated with the coating being studied, while the other remains bare as a control for AO flux calibration. Reference 8 contains full details of how the AO flux is estimated using the time history of oxidation of bare silver.

Instrumentation

The Los Alamos National Laboratory (LANL) O-atom simulation facility was used in the exposures of all samples. The LANL facility is capable of producing neutral AO in the hyperthermal energy range (1-5 eV) and at accelerated fluxes (10 to 100X actual LEO conditions).⁽⁸⁾ The estimated O-atom flux and energy for the exposures reported in this paper was 1×10^{17} atoms/cm²-sec at 2.1 eV, using an Ar/O₂ gas mixture for the beam. The dissociation of O₂ molecules into neutral O atoms was estimated to be >90%. These beam parameters (energy, dissociation) are slightly greater than those reported in reference 8 due to a larger nozzle diameter (0.016").

The electrical resistance of the silver sensors was measured using a digital multimeter, and sample temperature was determined using a thermocouple mounted on the sample holder. Samples were mounted with excellent thermal contact to the holder. Electrical resistance and sample temperature as a function of time during O-atom exposure were recorded and stored in a computer for later analysis.

Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) were performed at Photometrics Microanalytical Laboratories (Huntington Beach, California), and transmission electron microscopy (TEM) was performed at the University of California at Irvine, Department of Biological Sciences (Irvine, California).

Sample Preparation

The aluminum oxide coatings were sputter-deposited at the McDonnell Douglas Space Systems Company (MDSSC-HB) Microelectronics Center using a Commonwealth Millatron Ion Beam Vacuum Evaporator with a 5 in. diameter Al_2O_3 target. The samples were loaded on a vertical rotating carousel track, and the Al_2O_3 was sputter-deposited at a rate of about $15\text{\AA}/\text{min}$ for a total thickness of 750\AA . The thickness was determined by performing both surface profilometry and ellipsometry on a witness sample.

The following is a list of the samples which were all coated with 750\AA Al_2O_3 during the same run:

- (1) Atomic oxygen sensors of Al_2O_3 -alumina substrates.
- (2) Atomic oxygen sensors of Al_2O_3 -sapphire substrates.
- (3) Bare Si wafers (control samples for thickness measurements).
- (4) Ag (250\AA) coated Si wafers.
- (5) NaCl tablets.

Two different substrates (alumina and sapphire) were used to obtain information on the effect of surface roughness on coating lifetimes. The alumina substrates had surface roughness on the order of $2\text{-}3\mu\text{m}$, whereas the sapphire substrates were much smoother, with surface roughness of $<0.05\mu\text{m}$.

RESULTS

Auger analysis of the $\text{Al}_2\text{O}_3/\text{Ag}$ coated silicon wafer samples showed that the atomic composition of the coating was close to the 40%Al/60%O ratio expected for Al_2O_3 . Depth profiles of several samples exposed at different temperatures up to 310°C (after a fluence of 7×10^{20} atoms/ cm^2) indicated a very slight but consistent increase (no more than 2%) in the oxygen atomic concentration after AO exposure. Whether silver oxide had formed after exposure could not be determined by the Auger depth profiles; the sputtering is likely to "blur" interfaces. Profiles of an unexposed sample and exposed (310°C) sample are provided in Figures 2 and 3. Optical and scanning electron microscope examination of the exposed (310°C) and unexposed $\text{Al}_2\text{O}_3/\text{Ag}$ coated Si wafer samples showed no signs of cracking in the coating. There were no detectable changes in the thickness of the coating after exposure. Thicknesses of AO exposed (25°C) and unexposed Al_2O_3 coated Si wafer samples were within $\pm 1\%$, as determined by ellipsometry.

The primary purpose of depositing the Al_2O_3 on NaCl (salt) tablets was to permit easy removal of the film for transmission electron microscopy (TEM). The NaCl tablets were dissolved in water, and the Al_2O_3 films were then collected on copper grids. The electron diffraction patterns indicated that the Al_2O_3 film was amorphous before (Figure 4) and after (Figure 5) AO exposure at both 40°C and 200 °C. TEM inspection of the film up to 40,000X magnification did not reveal any obvious porosity or pattern of defects in the film, although the Al_2O_3 coating did replicate the surface features of the underlying salt tablet (Figure 6). These features included grain boundaries, polishing scratches and etch pits which were produced on the salt prior to film deposition.

Atomic oxygen penetration through the thin-film Al_2O_3 was evaluated using the AO sensors by measuring the electrical resistance of the silver underneath the coating. Control experiments were performed by heating the samples (with both alumina and sapphire substrates) in the absence of a beam and by exposing the samples to a pure Ar beam of hyperthermal energy to verify that the resistance changes in the silver were due to exposure to the O-atom beam and not simply due to heating of the silver film. During the exposures at any given temperature, sample temperatures were maintained within $\pm 5^\circ\text{C}$.

Data from the Al_2O_3 coated silver sensors using the relatively rough alumina substrates indicated significant scatter in the coating lifetimes. Large variations in fluence lifetime data for thin-film SiO_2 and Al_2O_3 coatings were also observed in our previous experiments.⁽⁹⁾ One sample exposed at 40°C showed a continuous increase in electrical resistance of the silver, which reached megohms after a total fluence of about 1.5×10^{21} atoms/cm² (Figure 7). Another sample exposed at the same temperature for similar fluence, however, exhibited less than a 10 ohm resistance change. An alumina sensor exposed at 100°C showed a higher rate of change in electrical resistance and a shorter coating fluence lifetime of 6.5×10^{20} atoms/cm².

For the smooth sapphire sensors, the electrical resistance data was converted to electrical conductance for estimation of the rate of conversion of the silver layers to silver oxide:

$$R = \frac{\rho l}{A} = \frac{\rho l}{wh}$$

R = electrical resistance

ρ = electrical resistivity

l = length of conductor

A = cross-sectional area of conductor

w = width of conductor

h = thickness of conductor

$$C = \frac{1}{R}$$

C = electrical conductance
(in mho when R is in ohms)

$$C = \mu h$$

μ = constant, assuming ρ , l and w to be constant

The electrical conductance of the silver at any given temperature was assumed to be linearly proportional to the thickness of the remaining silver, with uniform oxidation of the silver layers. The electrical conductance of silver oxide was assumed to be negligible in comparison to that of elemental silver. The rate of change of conductance, therefore, was used to estimate the rate of oxidation of the silver.

Data from the smooth sapphire sensors showed that there is oxygen penetration or diffusion through the Al_2O_3 coating upon exposure. A steady linear decrease in the conductance as a function of exposure time was seen for all samples tested at ambient temperature (40°C). Steeper slopes in the conductance vs. time curves were observed for all exposures at higher temperatures, indicating that temperature did have a marked effect on the rate of oxidation of the silver films. A permanent increase in electrical resistance after O-atom exposure was noted in all of the samples tested.

None of the coatings on the sapphire sensors "failed" - experienced an electrical resistance increase in the silver to megohms - as was the case in some of the rough alumina sensors. There was, however, variability in the decrease of conductance as a function of time at ambient temperature for the smooth sapphire sensors also, suggesting that there was some variability in the coatings. Each sample tested was exposed to the O-atom beam at ambient temperature prior to being exposed at an elevated temperature. Figure 8 shows the conductance vs. O-atom fluence profile for one sample which was exposed at 40°C for 2.5 hours, heated to 100°C while in the beam, and subsequently exposed at 100°C for 2 hours. Figure 9 shows the conductance vs. O-atom fluence profile for another sample which was exposed at 40°C for 7 hours, heated to 160°C while in the beam, and subsequently exposed at 160°C for 2 hours.

Optical and SEM analyses were performed on the sapphire sensors after AO exposure to determine if there was cracking in the Al_2O_3 films. Coating defects were detected in some, but not all, of the samples. Small cracks on localized areas of the coating (about 2% of total area) were detected (at 100X magnification) on one of the sensors (exposed at 40°C and 160°C), but no visible discoloration of the underlying silver outside the small cracked areas was seen. Another sapphire sensor had a pinhole-like defect in the coating, and discoloration of the silver around the defect was observed. The conductance vs. O-atom fluence curve for this sample showed a large initial decrease in conductivity upon exposure, but the slopes of the linear portion of the curve at both 40°C and 100°C were similar to those of another sample exposed at those temperatures which did not have any detectable defects.

Table 1 lists the slopes of the conductance vs. time curves for the sapphire sensors tested. Slope values for the higher temperature exposures were normalized to that of the ambient temperature exposures and the natural log (ln) of the slope was then plotted vs. $1/T$ (K^{-1}) to estimate the activation energy (Figure 10). An apparent activation energy for O-atom diffusion through the amorphous Al_2O_3 coating was calculated to be 5.2 kcal/mole.

Table 1. Slopes of Conductance vs. Time Curves for Sensors Tested

Sample	Temperature (°C)	Slope (mho/sec x 10 ⁻⁶)	Normalized Slope
1	40	-0.64	1.00
	100	-0.93	1.46
2	40	-1.33	1.00
	100	-3.70	2.79
3	40	-1.34	1.00
	100	-3.52	2.62
4	40	-0.59	1.00
	160	-6.79	11.55

DISCUSSION

Our experimental data indicates that there is some diffusion of AO through thin-film (750Å) sputtered Al₂O₃. The role which microscopic defects in the film play in the penetration of O-atoms through the coating needs further investigation, although diffusion was seen to occur even in the absence of detectable defects. O-atoms may be penetrating these films through a combination of processes. The apparent activation energy of 5.2 kcal/mole is unusually low for solid-state diffusion processes. Reported activation energies ranged from about 50 kcal/mole to 150 kcal/mole (at 1300-1800°C) in oxygen diffusion through single crystal and polycrystalline aluminum oxide, with the oxygen diffusion coefficient in polycrystalline aluminum oxide almost two orders of magnitude larger than that of single-crystal samples.⁽¹¹⁾

The effect of O-atom kinetic energy on O-atom diffusion through these films is unclear. Experiments at NASA/LeRC⁽¹²⁾ with thermal energy (<0.1 eV) AO has shown that there was some diffusion of oxygen into thin-film SiO₂. SiO₂ coatings (about 600Å) were deposited using reactive sputtering of ¹⁸O with Si, and the films were then exposed to a plasma environment with ¹⁶O. Enriched ¹⁶O concentration was seen in the films after exposure to a depth of about 300 angstroms. Exposure of sputtered Al₂O₃/Ag coated Si wafers in an oxygen plasma device at the University of Nebraska also showed increases in the silver oxide thickness with exposure time, as measured by variable angle spectroscopic ellipsometry.⁽¹³⁾ The exposure environment in plasma devices, however, contains oxygen ions and is not well-characterized. The reactivity observed may be due to charged particles (O⁺).

How the deposition process affects the microstructure, impurity concentration, density and subsequently, AO resistance of these thin-films is uncertain. Eliminating variability in the coatings is difficult; variability was observed in our results even under

well controlled conditions, with very smooth substrate surfaces. Thin-film coatings deposited on the smooth sapphire substrates offered significantly better protection than those deposited on the rough alumina substrates. If thin-film coatings are to be applied on spacecraft hardware, surface preparation of parts prior to coating may be a key factor in protection of the substrates. Thicknesses substantially greater than 750Å may also be required.

Work will be undertaken to evaluate how O-atom kinetic energy influences diffusion rates. Experiments will continue at LANL and will also be conducted in a flowing afterglow apparatus (thermal energy neutral AO environment)⁽¹⁴⁾ at Johnson Space Center.

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REFERENCES

1. Leger, L., Visentine, J., and Santos-Mason, B., "Selected Materials Issues Associated with Space Station," Proceedings from the 18th International SAMPE Technical Conference (1986).
2. Visentine, J.T., Leger, L.J., Kuminecz, J.F., and Spiker, I.K., "STS-8 Atomic Oxygen Effects Experiment," AIAA paper 85-0415 (1985).
3. Slomp, W.S., Santos-Mason, B., Sykes, G.F., and Witte, W.G., "Effects of STS-8 Atomic Oxygen Exposure on Composites, Polymeric Films, and Coatings," AIAA paper 85-0421 (1985).
4. Peters, P.N., Linton, R.C., and Miller, E.R., "Results of Apparent Atomic Oxygen Reactions on Ag, C, and Os Exposed During the Shuttle STS-4 Orbits," Geophys. Res. Lett., 10, 569 (1983).
5. Banks, B.A., Mirtich, M.J., Rutledge, S.K., Swec, D.M., and Nahra, H.K., "Ion Beam Sputter-Deposited Thin-Film Coatings for Protection of Spacecraft Polymers in Low Earth Orbit," AIAA paper 85-0420 (1985).
6. Gulino, D.A., Dever, T.M., and Banholzer, W.F., "Chemical Vapor Deposited Silica Coatings for Solar Mirror Protection," AIAA paper 88-0027 (1988).
7. Klemberg-Sapieha, J.E., Wertheimer, M.R., and Zimcik, D.G., "Plasma Deposited Multi-Purpose Protective Coatings for Space Applications," Proceedings from the 4th International Symposium Spacecraft Materials in Space Environment (1988).
8. Cross, J.B. and Blais, N.C., "High Energy/Intensity Atomic Oxygen Beam Source for Low Earth Orbit Material Degradation Studies," Proceedings from the 16th International Symposium on Rarefied Gas Dynamics (1988).
9. Cross, J.B., Lan, E.H., and Smith, C.A., "Evaluation of Coatings for Atomic Oxygen Protection in Low Earth Orbit," Proceedings from the 4th International Symposium Spacecraft Materials in Space Environment (1988).
10. Cross, J.B., Lan, E.H., and Smith, C.A., "A Technique to Evaluate Coatings for Atomic Oxygen Resistance," Proceedings from the 33rd International SAMPE Technical Conference (1988).
11. Oishi Y. and Kingery, W.D., "Self-Diffusion of Oxygen in Single Crystal and Polycrystalline Aluminum Oxide," J. Chem. Phys. 33, 480 (1960).
12. Gulino, D.A., Kren, L.A., and Dever, T.M., "Isotopic Study of Oxygen Diffusion in Oxide Coatings," 16th International Conference on Metallurgical Coatings (1989).

13. De, B.N., Ianno, N.M., Woollam, J.A., Gulino, D.A., and Dever, T.M., "Atomic Oxygen Effects on ITO, Ag and $\text{Al}_2\text{O}_3/\text{Ag}/\text{Si}$ as Studied by Ellipsometry," 1989 Materials Research Society Spring Meeting (1989).
14. Koontz, S.L., Kuminecz, J., Leger, L., and Nordine, P., "Materials Selection for Long Life in LEO: A Critical Evaluation of Atomic Oxygen Testing with Thermal Atom Systems," 15th Space Simulation Conference (1988).

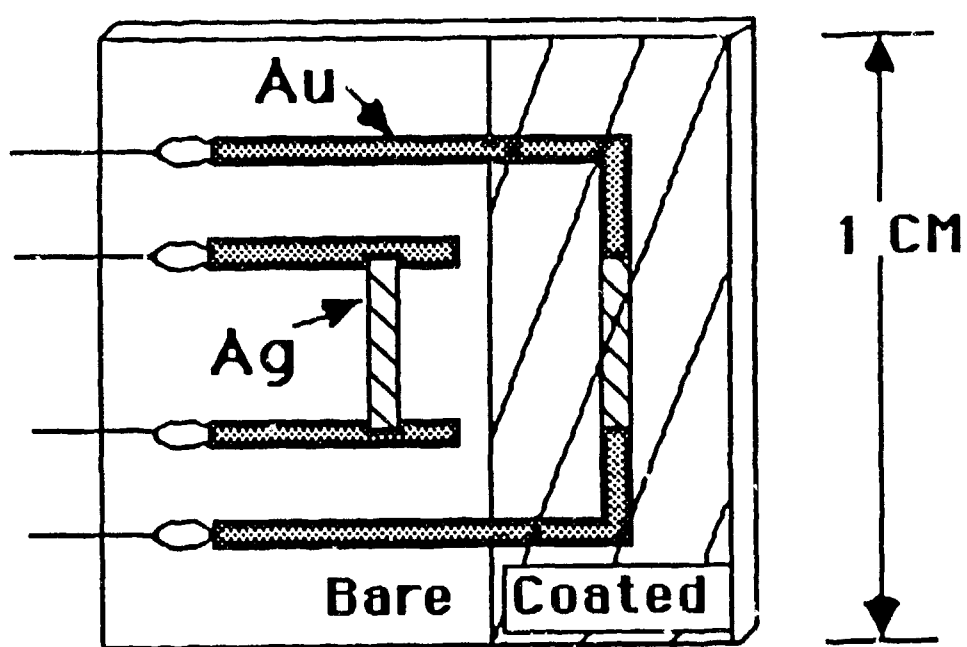


FIG. 1. Diagram of the atomic oxygen sensor. The thickness of the silver is 250\AA , and substrates are made of sapphire or alumina.

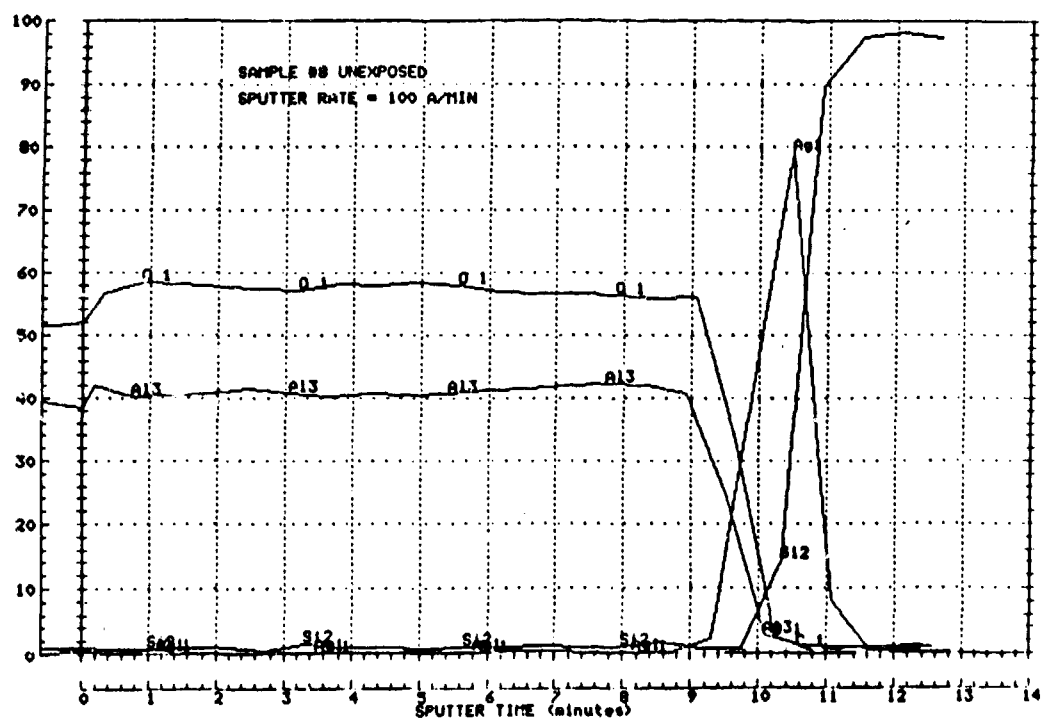


FIG. 2. Auger depth profile of an $\text{Al}_2\text{O}_3/\text{Ag}$ coated Si wafer sample which was unexposed.

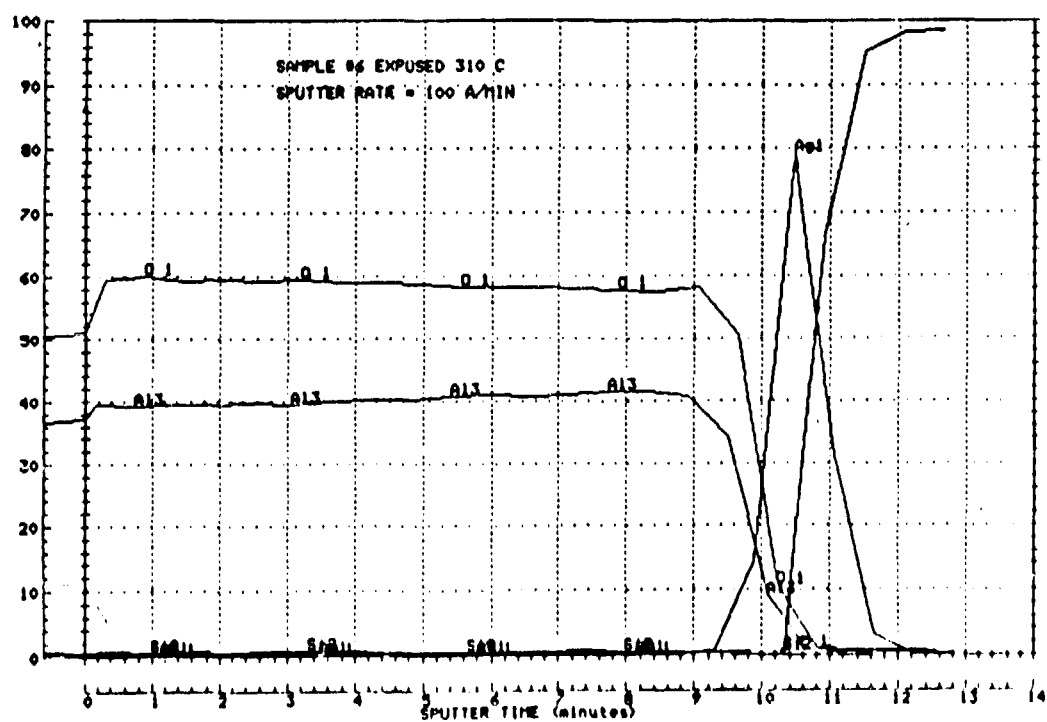


FIG. 3. Auger depth profile of an $\text{Al}_2\text{O}_3/\text{Ag}$ coated Si wafer sample which was exposed at 310°C for 7×10^{20} atoms/cm² atomic oxygen fluence.



FIG. 4. Electron diffraction pattern from transmission electron microscopy of an unexposed 750 Å Al_2O_3 film, indicating that the film was amorphous.



FIG. 5. Electron diffraction pattern from transmission electron microscopy of a 750 Å Al_2O_3 film which was exposed at 200°C for 2×10^{21} atoms/cm² atomic oxygen fluence. The film remained amorphous after exposure.

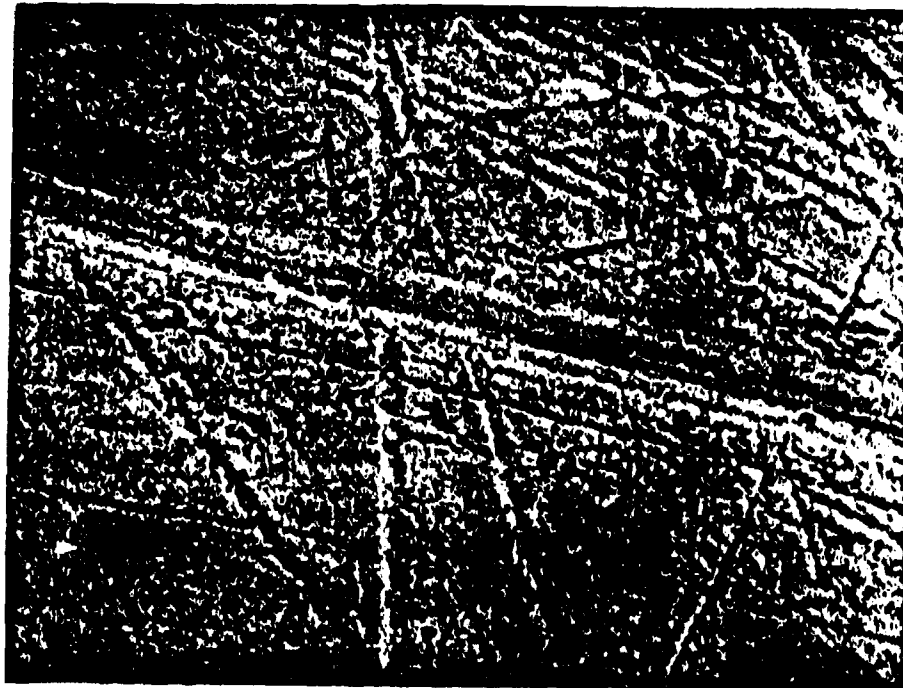


FIG. 6 Transmission electron microscopy photograph (10,000X magnification) of the Al_2O_3 film after exposure to 2×10^{21} atoms/cm² atomic oxygen fluence at 200°C. The Al_2O_3 film replicated the surface features (scratches, etch pits) of the NaCl tablet on which it was originally deposited.

Resistance of Ag Under 750Å Al_2O_3 - Rough Alumina Substrate - Exposure at 40°C

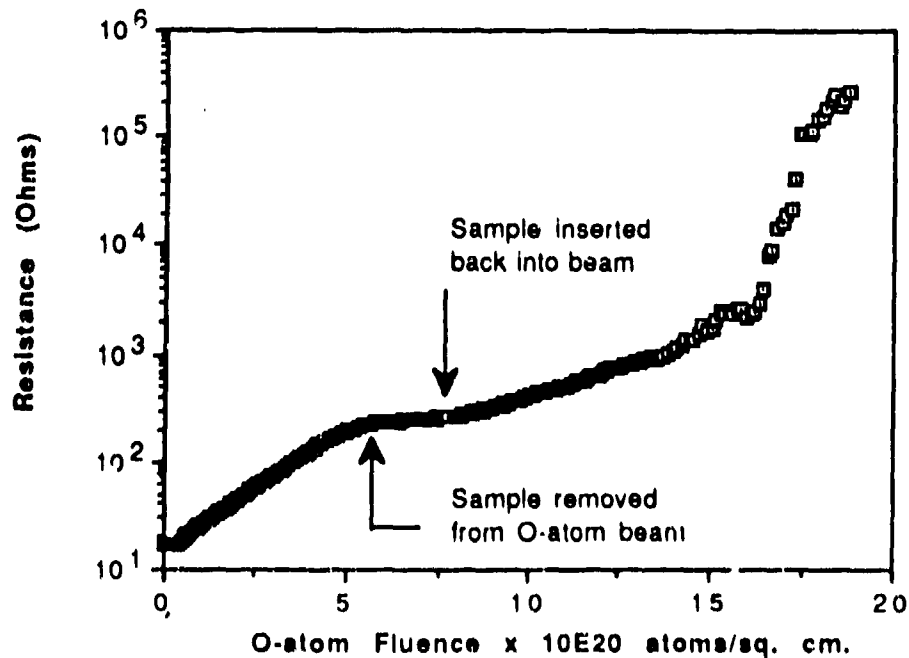


FIG. 7. Electrical resistance of a 750Å Al_2O_3 coated Ag strip on a rough alumina sensor as a function of O atom fluence. The sample was exposed at 40°C, and was removed from the O-atom beam for a short period during the run. The electrical resistance increase was dramatically slowed when the sample was removed from direct O-atom exposure.

**Conductance of Ag Under 750Å Al₂O₃
- Smooth Sapphire Substrate -**

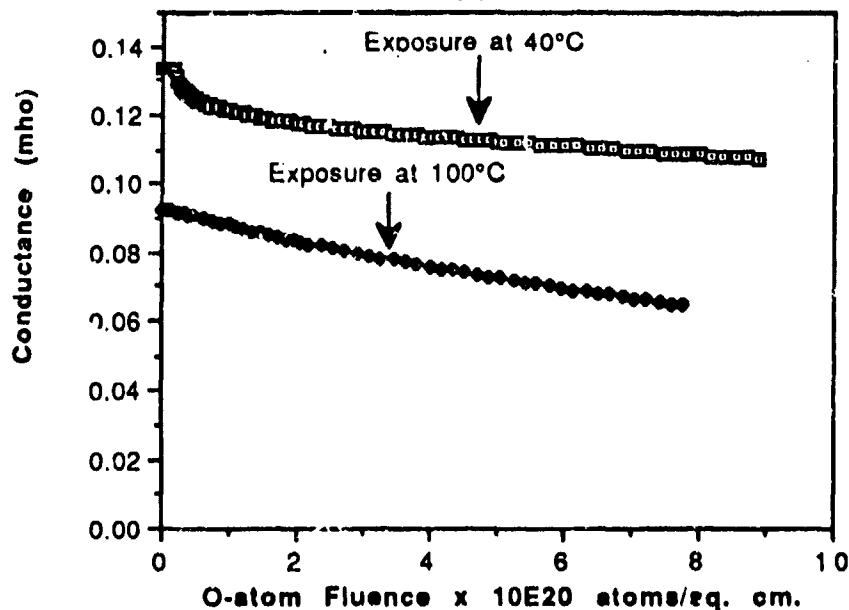


FIG. 8. Electrical conductance of a 750Å Al₂O₃ coated Ag strip on a smooth sapphire sensor as a function of O-atom fluence. The sample was first exposed at 40°C, heated to 100°C while in the beam, and exposed again at 100°C. The ratio of the slope_{100°}/slope_{40°} was 2.79.

**Conductance of Ag Under 750Å Al₂O₃
- Smooth Sapphire Substrate -**

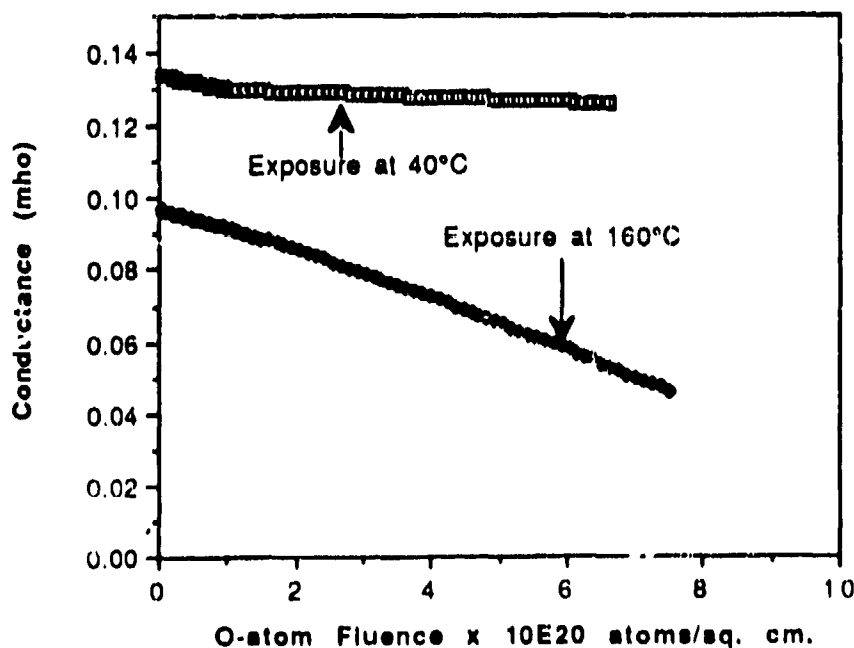


FIG. 9. Electrical conductance of a 750Å Al₂O₃ coated Ag strip on a smooth sapphire sensor as a function of O-atom fluence. The sample was first exposed at 40°C, heated to 160°C while in the beam, and exposed again at 160°C. The ratio of the slope_{160°}/slope_{40°} was 11.55.

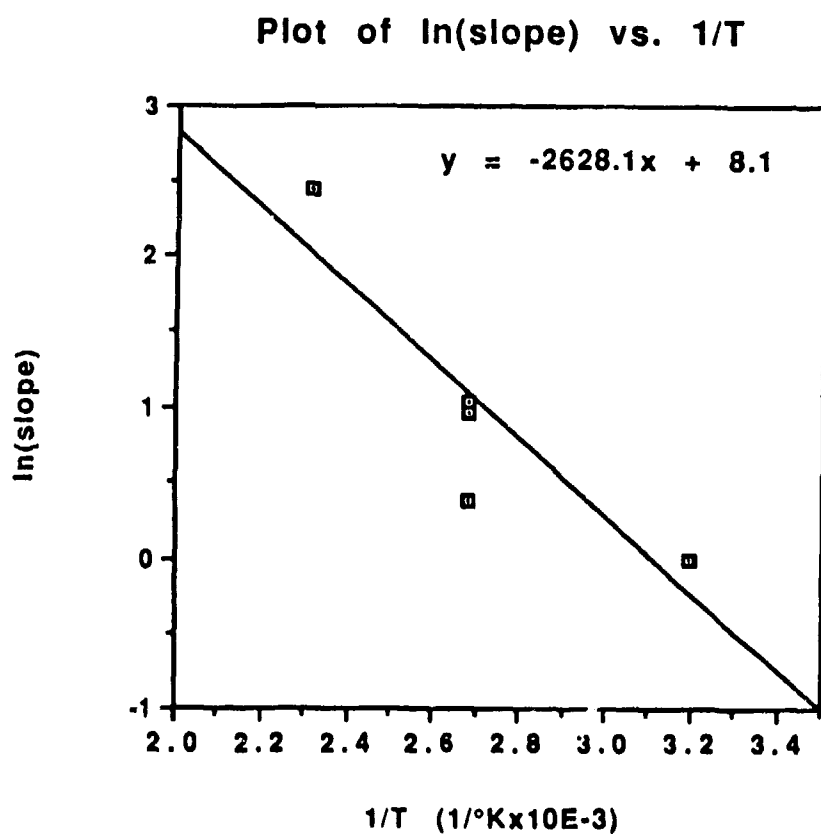


FIG. 10. Plot of $\ln(\text{slope})$ vs. $1/T$ for calculation of activation energy. E_a was found to be 5.2 kcal/mole.